



TITLE:

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CITATION:

Ishibashi, Masayoshi ...[et al]. Ultraviolet Spectrophotometric Determination of Tin (IV) as Chloro-Complex. Bulletin of the Institute for Chemical Research, Kyoto University 1959, 37(1): 38-47

ISSUE DATE:

1959-03-25

URL:

<http://hdl.handle.net/2433/75685>

RIGHT:

Ultraviolet Spectrophotometric Determination of Tin (IV) as Chloro-Complex

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Received January 6, 1959

The ultraviolet spectrophotometric determination of quardrivalent tin was studied. In the hydrochloric acid medium this metal exists as chloro-complex ion. The absorption spectra were investigated under various hydronium and chloride ion concentration. It was found that not only chloride ion but also hydronium ion gives large effect to the absorption spectrum of tin (IV), and some discussion was done on the relation between absorption spectrum and ionic species of tin chloro-complexes.

A method for spectrophotometric determination of tin (IV) was then studied using mixed solution of hydrochloric acid and magnesium chloride as reagent. Effects of the temperature, time of standing, and diverse ions were investigated. The calibration curve was obtained in the range of 0.1-10.0 p. p. m., and it was confirmed that the Beer's law is obeyed. The presented method is simple in procedure and have a considerably high accuracy, but it has the defect of having too many interfering ions.

INTRODCUTION

The absorptiometric determination of metal using mineral acid has the feature of inneccesity of a special coloring reagent, such as organic reagent, besides having the merits of simplicity of operation and of giving comparatively good accuracy. Several works have been recently reported about the spectrophotometric determination of various metals such as iron (III),¹⁾²⁾¹²⁾ lead³⁾⁴⁾ and bismuth⁴⁾ in which sulfuric,⁵⁾⁶⁾¹²⁾ perchloric,⁷⁾⁸⁾⁹⁾ hydrochloric¹⁾⁸⁾ and acetic acid¹⁰⁾ were used as reagents, respectively. These methods are based on the absorbance measurement at maximum wave length of absorption band which is considered to be due to the complexes formed between metallic ion and anion such as sulfate, hydroxy, chloride and acetate ion.

There are, however, few literatures on the studies about the spectrophotometric determination of tin by mineral acid, except that of Nielsh and Böltz¹¹⁾ in which hydrobromic acid was used as reagent. Desesa and Rogers have suggested, on the other hand, the possibility of the ultraviolet spectrophotometric determination of tin (IV) with hydrochloric acid in his investigation concerning the interference in the spectrophotometric determination of iron with hydrochloric acid.¹⁾

The present paper is concerned with the investigation of the absorption spectra of tin (IV) in the chloride medium and with the application of their results to the spectrophotometric determination of tin (IV).

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EXPERIMENTAL AND RESULTS

Apparatus and Materials

All absorbance measurements were performed with a Beckman Quartz Spectrophotometer, Model DU, with 1 cm silica transmission cells.

Tin solution: A stannous chloride solution, obtained by dissolving 5.000 gr. of pure metallic tin in the possibly small amounts of the concentrated hydrochloric acid, was oxidized to stannic state by absorbing chlorine gas into the solution. The oxidation was complete when the initial colorless solution became pale yellow due to excess of chlorine. The solution was then heated on a water bath to expell free chlorine untill the solution become again colorless, and it was diluted to exactly 500 ml with 1 to 1 hydrochloric acid solution. 10 ml of the above solution was pipetted into a 500 ml of volumetric flask and then diluted to the mark with hydrochloric acid (1 : 1). In the resulting solution the concentration of tin should be 200 p. p. m., but it was confirmed, in order to make sure, by gravimetric determination as stannic oxide. It was also ensured that the solution did not contain tin (II), iron (III) or free chlorine by giving negative test for the reaction such as molybdenum blue, red coloring of iron thiocyanate complex, or blue coloring due to the oxidation of iodide by potassium iodide starch paper, respectively. All the solutions for absorbance measurements were prepared by diluting the required quantity of the stock solution.

The hydrochloric acid was purified by distillation untill it gave negative test for iron. All other reagents, such as magnesium chloride, sodium chloride, and perchloric acid which were used for the adjustment of the chloride or hydrogen ion concentration, were analytical grade one.

Absorption Spectra

All absorbance measurements were carried out for the concentration of 10.0 p. p. m. of tin (IV), and with respect to reference solution of equivalent chloride and hydronium ion concentration.

Fig. 1 shows a series of the absorption spectra of stannic chloride in various concentration of hydrochloric acid. It is observed that the absorption maximum in the range of the wave length longer than 210 $m\mu$ appeared when the acid concentration was higher than 4 N and the absorption band shifted to longer wave length with the hydrochloric acid concentration. The position of maximum is 215 $m\mu$ for 4.2 N but is 233 $m\mu$ for 9.1 N of hydrochloric acid. The absorbance was also increased with the acid concentration. These bathochromic and hyperchromic effects with the hydrochloric acid are presumably due to the successive formation of the stannic-chloro complexes from lower to higher with increasing concentration of the hydrochloric acid.

In order to evaluate separately the effect of hydronium ion and chloride ion, the respective spectra of tin were obtained for solution having a constant hydronium ion concentration but varying chloride concentration. Other solution having constant chloride concentration but varying acidity were also studied. The absorption curves are shown in Fig. 2-6, and to understand clearly the cor-

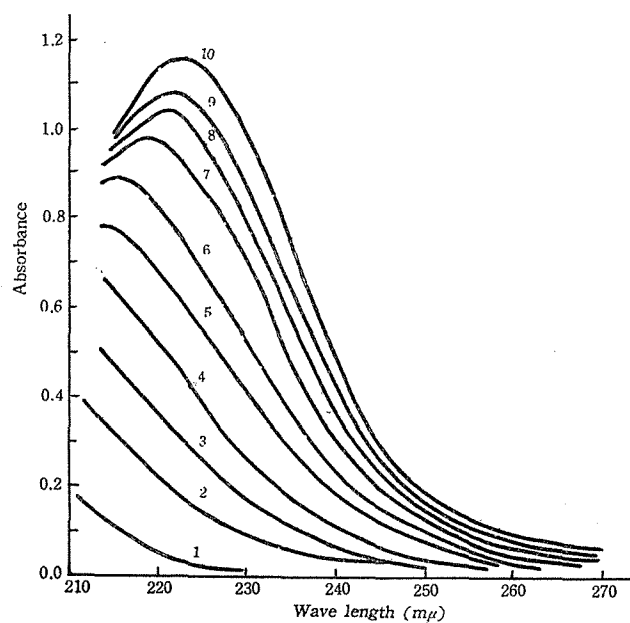


Fig. 1. Absorption spectra of tin in hydrochloric acid.

1, 0.3 N-HCl ; 2, 1.2 N-HCl ; 3, 2.2 N-HCl ; 4, 3.2 N-HCl ; 5, 4.2 N-HCl ;
6, 5.1 N-HCl ; 7, 6.1 N-HCl ; 8, 7.1 N-HCl ; 9, 8.1 N-HCl ; 10, 9.1 N-HCl.

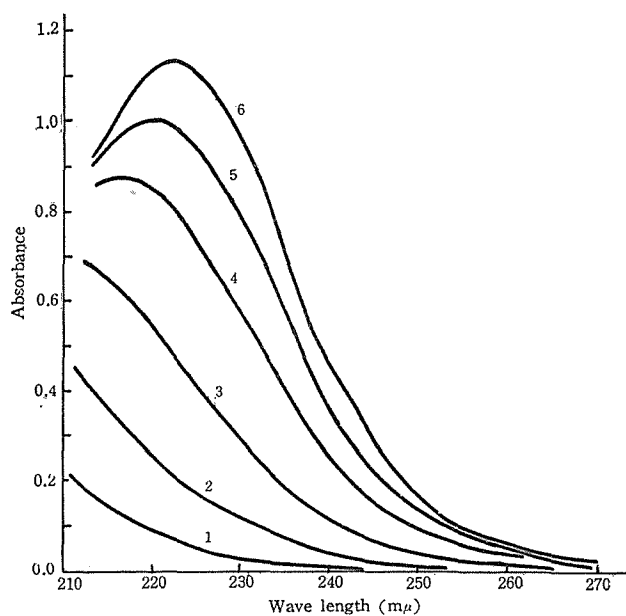


Fig. 2. $H^+=1.2 N$.

1, 0.3 M-Cl⁻ ; 2, 1.2 M-Cl⁻ ; 3, 3.1 M-Cl⁻ ; 4, 5.1 M-Cl⁻ ; 5, 6.5 M-Cl⁻ ;
6, 8.4 M-Cl⁻.

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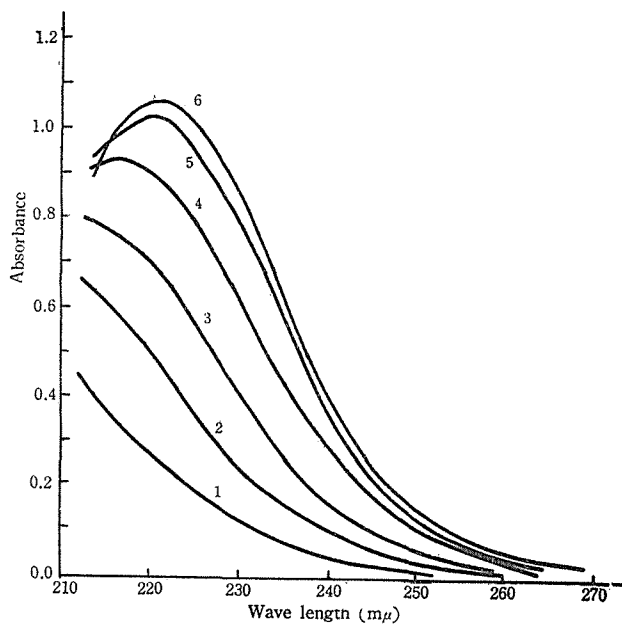


Fig. 3. $H^+=4.4\ N$.

1, 0.3 $M\text{-Cl}^-$; 2, 1.1 $M\text{-Cl}^-$; 3, 3.6 $M\text{-Cl}^-$; 4, 5.4 $M\text{-Cl}^-$; 5, 7.2 $M\text{-Cl}^-$;
6, 8.1 $M\text{-Cl}^-$.

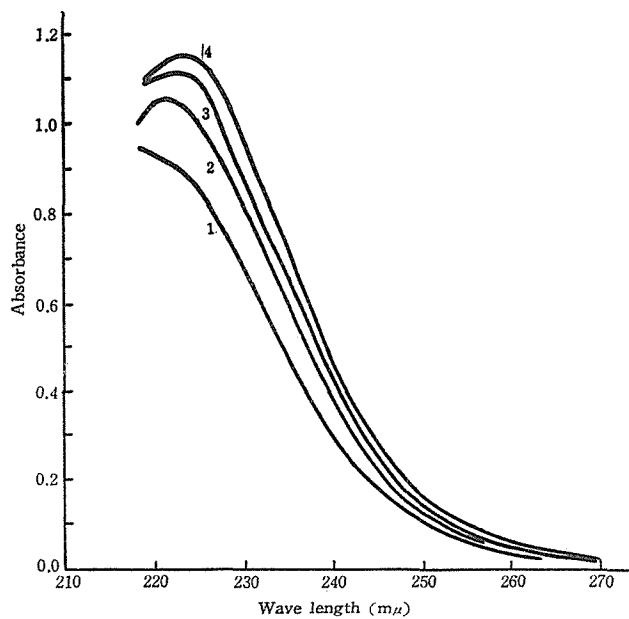


Fig. 4. $H^+=9.4\ M$.

1, 0.3 $M\text{-Cl}^-$; 2, 3.1 $M\text{-Cl}^-$; 3, 5.0 $M\text{-Cl}^-$; 4, 9.1 $M\text{-Cl}^-$.

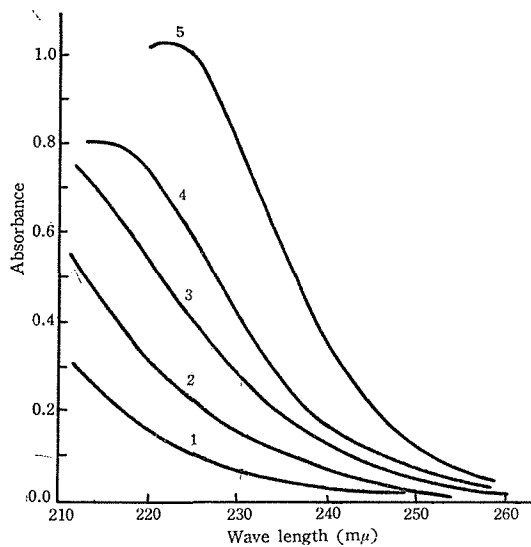


Fig. 5. $\text{Cl}^- = 1.2 \text{ M}$.

1, 0.3 NH^+ ; 2, 2.2 NH^+ ; 3, 4.1 NH^+ ; 4, 6.0 NH^+ ; 5, 8.9 NH^+ .

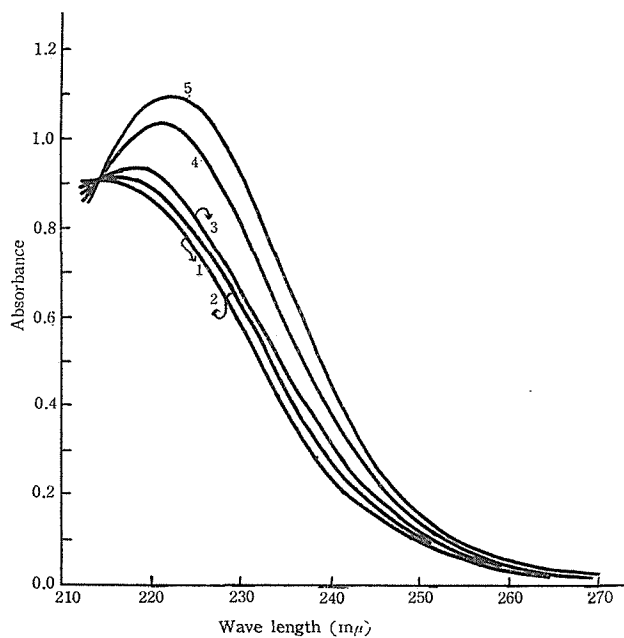


Fig. 6. $\text{Cl}^- = 6.0 \text{ M}$.

1, 0.3 N-H^+ ; 2, 2.7 N-H^+ ; 3, 6.0 N-H^+ ; 4, 7.4 N-H^+ ; 5, 9.4 N-H^+ .

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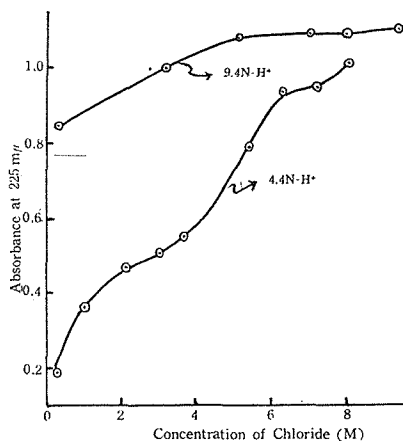


Fig. 7-a. Correlation between the absorbance at 225 μ and the concentration of chloride ion at constant acidity.

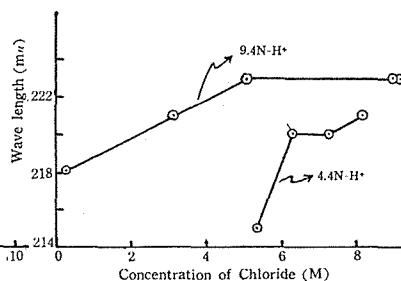


Fig. 7-b. Correlation between the maximum wave length and the concentration of chloride ion at constant acidity.

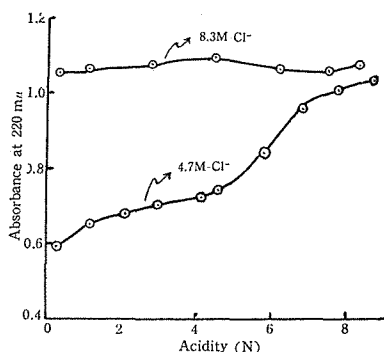


Fig. 7-c. Correlation between the absorbance at 220 and acidity at the constant concentration of chloride ion.

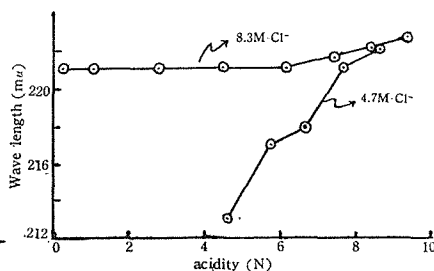


Fig. 7-d. Correlation between the maximum wave length and acidity at the concentration of chloride ion.

Fig. 7. Effect of the concentration of chloride ion concentration and acidity on the absorbance and maximum wave length of the system.

relation of the effects of hydronium and chloride ion to the absorption spectra, in Fig. 7 are shown the changes either in the absorbance at a given wave length or in the maximum wave length plotted against both the hydronium and chloride concentration. The results are summarized as follows.

Not only the chloride ion but also the hydronium ion give large effect to the system. At constant acidity, an increase in chloride concentration increased the intensity of the absorbance and shifts the maximum to longer wave length. At constant chloride concentration, the concentration of hydronium ion gives large effects to both the intensity of absorbance and the position of maximum wave length when the chloride concentration is lower, but its effect is less pronounced if the chloride concentration is higher. The position of peak shifts to longer wave length contaneously with the increase of hydronium ion when the chloride ion is hold in moderately lower concentration such as 4.7 M, but if the chloride

is very concentrated as 8.3 M it remains practically at constant wave length of 221 $m\mu$ as the hydronium ion concentration was varied between 0.3 and 6.2 M and in more concentrated acidity the peak shifts slightly to longer. At extreme higher acidity as 9.4 N, no effect was observed on the peak at 223 $m\mu$ and on the absorbance when the chloride ion is varied from 5 to 9 M.

According to Neumann,¹³⁾ in the case of pentavalent antimony in hydrochloric acid solution, $SbCl_6^-$ predominates in 9 M hydrochloric acid, $Sb(OH)Cl_5^-$ in 8 M acid, $Sb(OH)_2Cl_4^-$ in 6 M acid and $SbCl_3(OH)^{-3}$ and more hydrolyzed forms in more diluted acid than in 5 M. It will not be so unreasonable to assume that the behaviour of quadrivalent tin may be similar to that of pentavalent antimony in such a medium as hydrochloric acid solution. It is therefore presumed that the spectrum with the peak at 223 $m\mu$ may be belonged to the highest chloro-complex having the formula of $SnCl_6^{--}$, and that of with the peak at 221 $m\mu$ to the complex $Sn(OH)Cl_5^{--}$. The reason of large effect of hydronium ion to the absorption spectra, when both the hydronium and chloride concentration is considerably low, may be attributed to promotive action of hydronium ion for the formation of chloro-complex from hydroxo-complex. The phenomena is very different from the case of lead, bismuth and iron (III), as previously described by Merrit and coworkers⁴⁾ or by us, in which the hydronium ion gave no or slight effect to their absorption spectra in the chloride solution.

Determination of Tin

From above results, for executing the determination of tin as chloro-complex, both hydronium and chloride ion concentration should be critically regulated. Because the effects of chloride and hydronium ion concentration to the absorbance were less pronounced, 6 M chloride concentration and 215 $m\mu$ were chosen as the working conditions (Fig. 6).

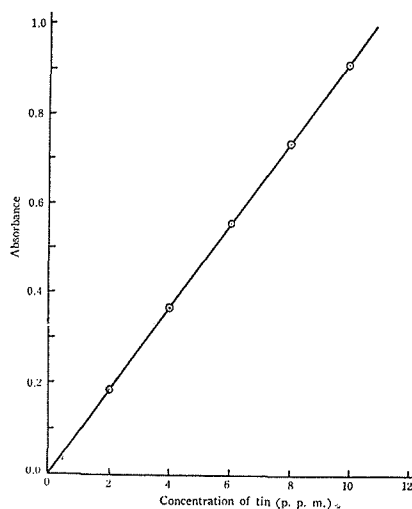


Fig. 8. Calibration curve at 215 $m\mu$.
Cl : 6.0M ; H⁺ : 1.5N ; T : 29C°.

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Calibration Curve

The standard procedure for the preparation of calibration curve is as follows.

Transfer 1.0, 2.0, 3.0, 4.0 and 5.0 ml of the standard solution having the concentration of 40 p. p. m. of tin with 6 M hydrochloric acid to a series of 20 ml volumetric flasks. Add appropriate amounts of 6 M hydrochloric acid so that each flask contains 5 ml of the acid and then after adding 10 ml of 9 M (perchloride ion) magnesium chloride solution, dilute to the mark with water. Measure the absorbance at 215 m μ with reference to the reagent blank solution. As shown in Fig. 8, Beer's law is obeyed up to 10.0 p. p. m.. In the following experiments, the solution was prepared by the same procedure as calibration curve.

Effects of Temperature

The effect of the temperature on the absorbance at 215 m μ was then investigated and the result are shown in Table 1. It is seen that the absorbance

Table 1. The effect of the temperature.

Temperature (°C)	Absorbance at 215 m μ (Sn 4.0 p. p. m., Cl ⁻ 6 M, H ⁺ 1.5 M)
43	0.400
41	0.398
39	0.383
37	0.372
36	0.366
35	0.362
34	0.360
32	0.350
29	0.320
27	0.312
21	0.306

increases with the temperature in the range 21-43°C. The temperature coefficient of absorbance is 0.0041/°C and this value is considerably high compared with the other cases such as iron or lead chloro-complexes. This result suggests that the equilibrium between the lower and higher tin chloro-complex shift markedly with temperature, that is, the degree of the complex formation is higher, the higher the temperature. It is, therefore, desirable to hold the temperature constant in a series of the experiments.

Stability

The stability of the system is then investigated for a week or more and it is resulted that the absorbance at 215 m μ did not change during these time.

Effect of Diverse Ions

A study was made on the effect of several cations, mainly being assumed to be co-distillated with tin and therefore being unable to be removed by distillation, and also some cations and anions which may be encountered commonly.

Measurements were made for the solutions containing a proper amount of foreign salt with 4 p. p. m. of tin (IV). The results obtained are shown in Table 2. Aluminum does not interfere when it present in the concentration of 2000 p.p.m., but other elements interfere seriously the determination of tin by giving the positive errors. Iron (III), vanadium (V), antimony (III), antimony (V), arsenic

Table 2. The effect of diverse ion.

Diverse ion		Form	Absorbance at 215 m μ (Sn : 4.0 p. p. m., Cl ⁻ : 6 M H ⁺ : 1.5 N)
			0.363
Fe (III)	5 p. p. m.	Alum	1.060
V (V)	5 "	Meta Vanadate	0.785
Sb (III)	5 "	Sulfate	0.517
Sb (V)	5 "	"	0.718
As (III)	5 "	Na-Arsenite	0.547
As (V)	5 "	Na-Arsenate	0.358
"	50 "	"	0.475
"	500 "	"	1.362
Al	2000 "	Alum	0.368
Ge (IV)	5 "	Na-Germanate	0.366
"	50 "	"	0.383
Ti (IV)	5 "	Sulfate	0.413
Se (IV)	5 "	Dioxide	0.414
ClO ₄ ⁻	0.5 N	HClO ₄	0.406
SO ₄ ²⁻	20000 p. p. m.	Na-Sulfate	0.395
"	100000 "	"	0.429
Br ⁻	10000 "	Na-Bromide	Large

(III), titanium (IV), and selenium (IV) give the positive value when they present in the same concentration as tin. Arsenic (V) and germanium (IV) interfere when their concentration. is ten fold of tin.

SUMMARY

(1) The absorption spectra of tin (IV) in the medium of variuos concentration of hydronium and chloride ion. It was found that the highest stannic chloro complex (SnCl₆²⁻) may have the absorption spectrum with the peak at 223 m μ and also the complex Sn(OH)Cl₅²⁻ with the peak at 221 m μ .

(2) The hydronium ion gives a large effect on the system, because it will expedite the formation of chloro-complex from stannic hydroxo-complexes which exist in low acidity.

(3) 6 M chloride concentration was recommended as working medium for the spectrophotometric determination of tin (IV), being the change in intensity of absorbance is slight with reagent concentration.

(4) Beer's law was obeyed up to 10 p. p. m. of the metal, measuring the absorbance at 215 m μ .

(5) The temperature coefficient of absorbance was 0.0041/°C.

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(6) Aluminum does not interfere, but some cations such as As (III, V), Sb (III, V), Fe (III), V (V) and Ti (IV) interfere remarkably.

REFERENCES

- (1) M. S. Desesa and L. Logers, *Anal. Chim. Acta*, **6**, 534 (1952).
- (2) M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi and K. Kitagawa, *Bull. Chem. Soc. Japan*, **29**, 57, (1956).
- (3) M. Ishibashi, Y. Yamamoto, and K. Hiroy, *Japan Analyst*, **7**, 582 (1958).
- (4) C. Merritt, H. M. Hershenson and L. B. Rogers, *Anal. Chem.*, **25**, 572 (1953).
- (5) H. L. Greenhaus, A. M. Feiluch and L. Gorden, *Anal. Chem.* **29**, 153 (1957).
- (6) M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi and T. Kitagawa, *Nippon Kagaku Zasshi*, **76**, 758 (1955).
- (7) R. Bastian, R. Weberling and F. Pallila, *Anal. Chem.*, **28**, 459 (1956).
- (8) M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi and T. Kitagawa *Bull. Chem. Soc. Japan*, **30**, 433 (1957).
- (9) M. Ishibashi, Y. Yamamoto and K. Hiroy, This Bulletin, **36**, 24 (1958).
- (10) M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi and K. Kitayama This Bulletin, **35**, 6 (1957).
- (11) W. Nielsh and G. Böltz, Z., *Anal. Chem.*, **142**, 94, 102, 109 (1954).
- (12) R. Bastian, R. Weberling, F. Pallilla, *Anal. Chem.* **25**, 284 (1953).
- (13) H. M. Neumann, *J. Am. Chem. Soc.*, **76**, 2611 (1954).